

## Vapor Density of Dieldrin

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■ Vapor density associated with solid-phase dieldrin (HEOD, 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo-exo-5,8-dimethanonaphthalene) and dieldrin-soil mixtures, measured by a gas-saturation technique, was three to 12 times greater than predicted from published vapor pressure values. The measured vapor densities at 20, 30, and 40° C. were 54, 202, and 676 ng. of HEOD per liter, respectively. The vapor density of HEOD in three dry dieldrin materials was the same as that of HEOD plus water. The vapor density of HEOD in soil at 100 p.p.m. was the same as that of HEOD without soil, but at 10 p.p.m. the vapor density in soil was reduced approximately 80%. The heat of vaporization of HEOD with or without soil was 23.6 kcal. per mole. The data indicate that the so-called "codistillation" phenomenon is not due to an increased vapor density in the presence of evaporating water and that loss of water is not required to attain maximum vapor density of HEOD, either in soil or over HEOD-water mixtures.

Considerable evidence (Bowman, Schechter, *et al.*, 1965; Edwards, 1966; Harris and Lichtenstein, 1961) indicated that volatilization from the soil surface may be an important pathway for loss of dieldrin and other relatively per-

sistent organochlorine insecticides. Acree (1963), Bowman, Acree, *et al.* (1959, 1964), and Bowman, Schechter, *et al.*, (1965) reported that loss of water contributed to the volatilization of DDT and other insecticides by an apparent "codistillation" process. They implied that loss of water was necessary for significant volatilization to occur from water or soil surfaces.

A project was recently initiated to evaluate factors affecting vapor-phase movement and volatilization losses of organochlorine compounds in soils. The attainment of this objective required the determination of factors affecting the relationship between the solid-phase concentration in soils and vapor density. Dieldrin vapor density in association with solid-phase dieldrin and dieldrin-soil mixtures is reported here. The results are compared with vapor densities calculated from vapor pressure values reported by Porter (1964), and implications to HEOD vapor species and rates of volatilization are discussed.

### Experimental

Vapor density of dieldrin (HEOD) in association with solid-phase dieldrin and dieldrin-soil mixtures was determined by a gas saturation method using high-purity dry nitrogen as a carrier gas in apparatus similar to that shown in Figure 1. In the gas saturation method a current of inert gas is passed through

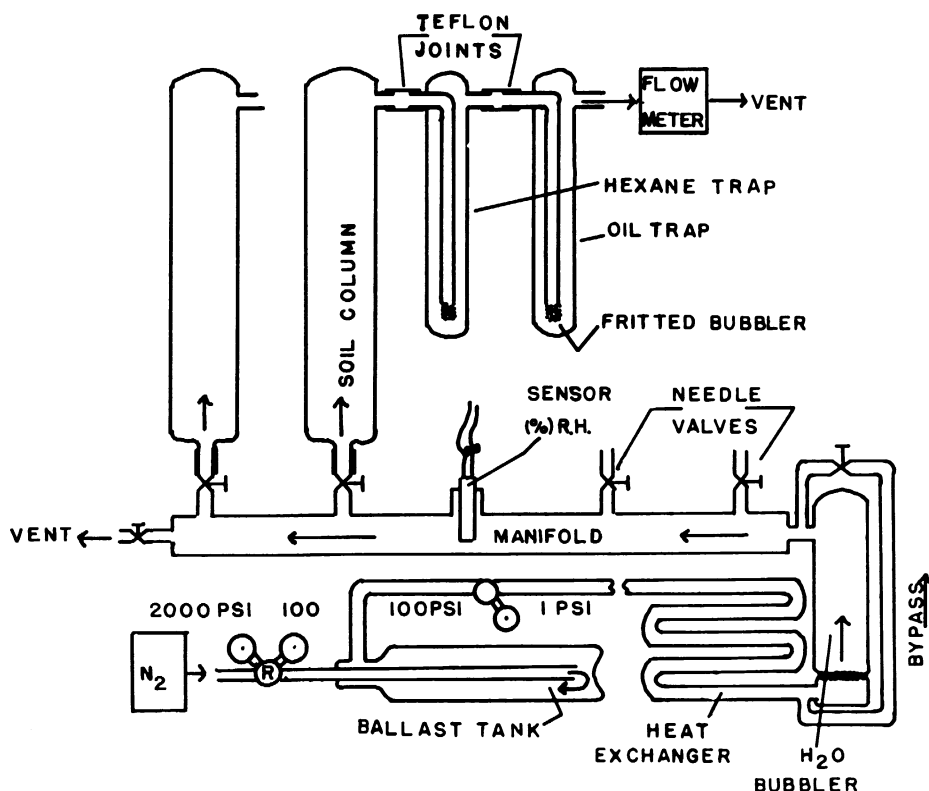


Figure 1. Schematic diagram of flow system used to determine dieldrin vapor density by the gas saturation method

or over the material at a sufficiently slow rate to ensure equilibrium saturation (Thompson, 1963). The entire apparatus, except the nitrogen supply tank, the high-pressure regulator, and the bubble-flow meter, were inside a constant temperature incubator. The assembly included a heat exchanger to bring the temperature of the  $N_2$  gas to the temperature of the incubator, a water bubble-chamber with bypass to adjust the humidity of the  $N_2$ , and a pressure regulator to maintain a constant pressure of 1 p.s.i. in the manifold. A relative humidity and temperature sensor was installed in the manifold and the flow of gas through the columns was regulated by needle valves. The humidity could be accurately controlled by adjusting the proportion of the nitrogen passing through the humidifying chamber and the amount of gas flowing out the relief valve at the end of the manifold.

The 6- × 43-cm. dieldrin-saturating columns were made from medium-wall borosilicate glass tubing capped with 60/50 Teflon joints. For soil-dieldrin mixtures the columns were mounted vertically as shown in Figure 1. For measuring vapor density of HEOD without soil the columns were mounted horizontally with the HEOD placed either in the bottom or coated on the sides of the columns. Vapor phase HEOD was removed from the slowly flowing  $N_2$  gas stream in hexane-oil traps consisting of two 250-ml. gas-washing bottles connected in series with Teflon tubing. The first trap contained 150 ml. of hexane which effectively removed all the HEOD. The second trap contained 150 ml. of transmission oil which trapped the hexane volatilized from trap 1. This was required to maintain a fairly constant liquid head and to prevent undue interference of hexane with the flow measurement in the bubble-flow meter.

To calculate vapor density in weight per unit volume of gas passing through the saturator, it was necessary to correct the measured volumes for pressure and temperature differences and for the net volume of hexane added to the nitrogen stream between the saturator and the flow meter. The traps were weighed to determine the amount of hexane passing through the flow meter. The flow meter was at ambient temperature; the saturator was at controlled temperatures and exposed to

slightly higher pressures due to resistance to flow through the fritted bubblers and the liquid head of the trapping medium. A mercury manometer was used to establish the pressure within the saturator. The value for the volume of  $N_2$  passing through the saturator was established from the measured volume by assuming that Dalton's law was valid for the hexane vapor lost to the gas stream and by correcting to the saturator temperature and pressure using the ideal gas laws. Additional information concerning these calculations can be found in Thompson (1963).

Recrystallized dieldrin, 99% HEOD (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo-exo-5,8-dimethanonaphthalene), obtained from Shell Chemical Co. was used as the dieldrin material in all studies except for some comparative measurements made with Shell Technical Dieldrin and analytical-grade dieldrin obtained from the Polyscience Corp. For vapor density of HEOD only, 1 gram of dieldrin was placed in the bottom of the saturator chamber. To determine the effect of water on vapor density of HEOD, measurements were made with 100 ml. of water sufficient to cover the dieldrin partially, in the bottom of the saturator.

The Gila silt loam used in these studies is a desert soil containing approximately 18.4% clay, 0.6 organic matter, with a surface area of approximately 90 sq. meters per gram and an exchange capacity of 18 meq. per 100 grams. The clay fraction is predominantly montmorillonite with lesser amounts of mica, quartz, and feldspars. In preparing columns, the soil was first autoclaved and exposed to moist air for several days before adding dieldrin. Sufficient dieldrin in 100 ml. of acetone for 10 or 100 p.p.m. HEOD was added to the soil and the soil thoroughly mixed. The soil was aerated with moist air to remove the acetone, then adjusted to 3.9% water content by adding a predetermined amount of water with an atomizer, mixing thoroughly, and equilibrating at 94% relative humidity. After the columns were packed with approximately 900 grams of treated soil, they were placed in an incubator at 30° C. for 30 days before measurements were initiated.

In the gas saturation method, when equilibrium between the

gas and solid phase is obtained, the amount of vapor trapped per unit time should vary linearly with the flow rate of the gas. In the present experiments, the flow rate of the  $N_2$  gas was varied between 1 and 300 ml. per minute with HEOD only in the saturator, and between 1.7 and 12.6 ml. per minute with the soil columns. Within these ranges of flow rates the HEOD vapor densities were independent of flow rate within the experimental error of the method. This made it unnecessary to control rigidly the flow rate, and only required monitoring it frequently enough to establish the total volume of gas flowing through the saturator during each run. The nitrogen gas flow rates remained essentially constant within each individual run, but rates from 3 to 6 ml. per minute were generally used to provide a total flow through the saturator of from 10 to 80 liters, depending upon the expected concentration of dieldrin in the  $N_2$  gas and the amount of dieldrin required for quantitative estimation. The HEOD content of the hexane was determined, after appropriate concentration in a Kuderna-Danish concentrator, by gas-liquid chromatography using a Beckman GC-5 equipped with a nonradioactive electron-capture detector. From three to nine measurements were made on each set of columns at each of three temperatures, 20, 30, and 40° C.

The possibility of entrainment and surface creep as a factor influencing measurements was investigated by measuring vapor density with and without a 4-foot coil of Teflon tubing between the saturator and hexane trap. The insertion of the 4-foot coil of tubing did not significantly affect measured vapor density values and was not used for the data reported herein.

## Results and Discussion

The vapor density and calculated vapor pressures of dieldrin (HEOD) with and without water are shown in Table I. The vapor density in association with dry HEOD was the same as that associated with HEOD plus water, indicating that the presence of water or evaporating water had no appreciable influence on the vapor density, or potential vaporization rate. Vapor density of HEOD in dry Shell Technical dieldrin and analytical grade dieldrin from the Polyscience Corp. was the same as that reported in Table I for dry HEOD at comparable temperatures.

Dieldrin vapor density increased markedly with temperature. The apparent vapor pressures were calculated from the vapor density,  $W/V$ , with the equation:

$$P = (W/V)(RT/M) \quad (1)$$

where  $R$  is the molar gas constant,  $T$  the absolute temperature, and  $M$  the molecular weight of HEOD assuming a monomer gaseous species.

Combining all "wet" and "dry" HEOD measurements resulted in a mean vapor density of 54, 202, and 676 ng. HEOD per liter equivalent to an apparent vapor pressure of  $2.6 \times 10^{-6}$ ,  $10.0 \times 10^{-6}$ , and  $34.7 \times 10^{-6}$  mm. of Hg at 20, 30, and 40° C., respectively. The following equation, graphically shown in Figure 2, relates this apparent vapor pressure to temperature:

$$\text{Log}_{10}P = 12.07 - (5178/T) \quad (2)$$

Porter (1964) reported the vapor pressure of HEOD to be  $0.78 \times 10^{-6}$ ,  $1.43 \times 10^{-6}$ , and  $2.74 \times 10^{-6}$  mm. of Hg at 20, 30, and 40° C., respectively. These values were obtained using an effusion technique (Porter, 1968). The measured vapor densities are from three to 12 times greater than would be predicted from Porter's "static" vapor pressure values.

The vapor density and calculated vapor pressure of HEOD in Gila silt loam soil in relation to temperature and concentration of HEOD are shown in Table II. For these measurements the soil-water content was 3.9% which, in Gila silt loam, is equivalent to 94% relative humidity, or approximately 90 bars matric suction. The humidity of the nitrogen carrier gas was in equilibrium with this moisture content, which resulted in no net loss of water from the soil column during the measurements. At 100 p.p.m. of HEOD in soil the vapor density was the same as that of HEOD without soil. Thus, a saturated vapor density was attained in soil, and Equation 2 adequately describes the linear relationship between  $\text{Log } P$  and  $1/T$  for this concentration. At 10 p.p.m. of HEOD, the vapor density was approximately 20% as great as that of HEOD without soil. Equation 3 expresses the linear relationship between  $\text{Log } P$  and  $1/T$  for 10 p.p.m. of HEOD:

$$\text{Log}_{10}P = 11.33 - (5170/T) \quad (3)$$

This relationship is graphically shown in Figure 2.

According to one form of the Clausius-Clapeyron equation, the slope ( $m$ ) of the line, when  $\text{Log}_{10}P$  is plotted vs.  $1/T$  is related to heats of vaporization by the equation:

$$\Delta H_v = -2.303Rm \quad (4)$$

where  $\Delta H_v$  is heat of vaporization in calories per mole when  $R$  is in calories per mole per degree. Since the slopes for ad-

Table I. Vapor Density and Calculated Vapor Pressures of Dieldrin (HEOD) with and without Water

	Temp., °C.	Vapor Density, Ng./L.	Vapor Pres- sure, <sup>a</sup> Mm. Hg $\times 10^{-6}$
HEOD (wet) <sup>b</sup>	20	52 $\pm$ 5 <sup>c</sup>	2.6
	30	199 $\pm$ 9	9.9
	40	685 $\pm$ 38	35.1
HEOD (dry)	20	59 $\pm$ 5	2.8
	30	205 $\pm$ 19	10.1
	40	661 $\pm$ 16	33.9

<sup>a</sup> Calculated from vapor density,  $W/V$  with the equation:  $P = \frac{W}{V} \cdot \frac{RT}{M}$  using 381 as the molecular weight ( $M$ ) of the gaseous species.

<sup>b</sup> With 100 ml. of water in the saturation chamber.

<sup>c</sup> The 95% confidence limit or  $2 \times$  standard error of the mean calculated for each series of runs.

Table II. Vapor Density and Calculated Vapor Pressure of HEOD in Gila Silt Loam Soil

HEOD Concn., P.P.M.	Temp., °C.	Vapor Density, Ng./L.	Vapor Pressure Mm Hg $\times 10^{-6}$
100	20	45 $\pm$ 3 <sup>a</sup>	2.2
100	30	205 $\pm$ 19	10.2
100	40	690 $\pm$ 17	35.4
10	20	10 $\pm$ 0.6	0.5
10	30	37 $\pm$ 3	1.9
10	40	130 $\pm$ 8	6.7

<sup>a</sup> The 95% confidence limit or  $2 \times$  standard error of the mean calculated for each series of runs.

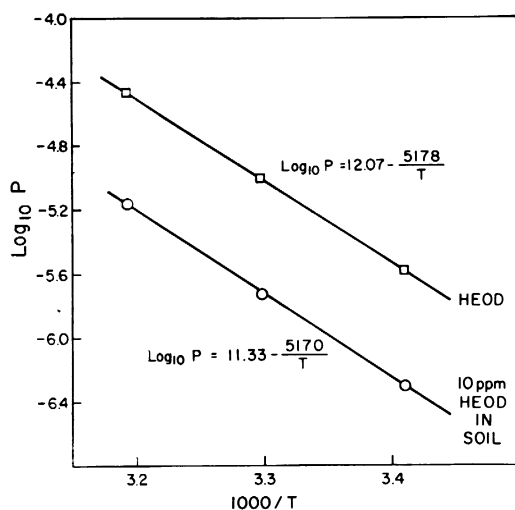


Figure 2. The relationship between apparent vapor pressure of HEOD and temperature

sorbed and unadsorbed HEOD are similar, heats of vaporization are also similar. Heats of vaporization for unadsorbed HEOD and for 10 p.p.m. of HEOD in soil, calculated with Equation 4, were 23.6 kcal. per mole.

Other relevant thermodynamic quantities were calculated from the change in vapor pressure with temperature using the following equations from Oster and Low's (1963) treatment of clay-adsorbed water:

$$\Delta H \text{ or } \bar{H}_a - H^0 = (\bar{H}_a - \bar{H}_v) - (H^0 - \bar{H}_v) = (\Delta H_v)^0 - (\Delta H_v)_a \quad (5)$$

$$\Delta F \text{ or } \bar{F}_a - F^0 = RT \ln (P_a/P^0) \quad (6)$$

$$\Delta S \text{ or } \bar{S}_a - S^0 = [(\bar{H}_a - H^0) - (\bar{F}_a - F^0)]/T \quad (7)$$

where  $\Delta H_v$  is the heat of vaporization of adsorbed or unadsorbed HEOD;  $H$ ,  $F$ , and  $S$  are the heat content, free energy, and entropy of the HEOD, respectively;  $R$  is the molar gas constant;  $T$  the absolute temperature,  $P$  is the vapor pressure of HEOD; the bars over the symbols designate partial molar quantities; the subscripts "a" and "v" refer to the adsorbed and vapor states; and the zero superscript refers to the standard state HEOD without soil at 30° C.

The change in free energy,  $\Delta F$ , on adsorption of HEOD at 10 p.p.m., calculated from the ratio of the vapor pressure of HEOD only vs. soil at 10 p.p.m. of HEOD, was -1000 calories per mole at 30° C. The change in entropy,  $\Delta S$ , due to adsorption of the HEOD at 10 p.p.m. calculated with Equation 7 using heats of vaporization calculated from the linear plot of  $\text{Log}_{10}P$  vs.  $1/T$  was +3.43 calories per degree per mole at 30° C. The entropy of the adsorbed state at 10 p.p.m. of HEOD was greater than the entropy of solid-state HEOD. Since a gain in entropy is related to a decrease in order, this would imply that adsorbed HEOD at 10 p.p.m. was less ordered than solid-state HEOD or HEOD at 100 p.p.m. in soil. A decrease in entropy on adsorption is usually observed as reported by Oster and Low (1963) for adsorption of water on clays.

The discrepancy in vapor density between that calculated from Porter's data and measured in our experiments could be

due to insufficient saturation of the atmosphere in the effusion measurements reported by Porter, or to association of HEOD molecules in the vapor state in the measurements reported herein using the gas saturation technique. To explain the discrepancy entirely on the latter basis would require molecular groupings of increasing size as the temperature increased, and assuming that the molecules were leaving the dieltrin surface as groups of molecules rather than as monomers. According to Lewis and Randall (1961), the mean molecular weight of the vapor species may be determined by comparing measured vapor densities with densities calculated from static vapor pressure values. Based on this comparison, the average number of molecules per associated group, or polymer size, needed to explain the discrepancy between measured and calculated vapor densities is 3.4, 7.0, and 12.7 at 20, 30, and 40° C., respectively. Groups of 3, 7, and 12 HEOD molecules would be approximately 12, 16, and 20 Å. in diameter, respectively. Bowman, Acree, *et al.* (1960) concluded that DDT was present in water as finely divided suspended particles rather than as a true solution of individual molecules. Dieltrin probably behaves similarly in water, and it is logical that the smaller groups of molecules may escape into the atmosphere from the air-water interface.

The increase in entropy on adsorption indicates that possibly the interaction with soil resulted in less association between molecules in the vapor state, probably due to breakdown of the HEOD into smaller molecular groups or into individual molecules on the surface of the soil clays. The altering of vapor species by interaction with various solids has been reported previously (Lewis and Randall, 1961).

The fact that the vapor density and heat of vaporization of dieltrin applied to soil at 100 p.p.m. is the same as pure HEOD indicates that the adsorption forces between dieltrin and soil are quite weak and probably the dieltrin is present as globules or is adsorbed at the air-water interface. When applied at rates of 100 p.p.m. or greater to a soil with even a small amount of water, dieltrin can vaporize initially from soil as easily as from pure HEOD; therefore, surface applications of dieltrin and probably other similar organochlorine insecticides will volatilize rapidly from the soil until the concentration at the surface falls somewhat below 100 p.p.m. To illustrate potential vaporization rates, at 30° C. and a flow rate of 300 ml. per minute, dieltrin vaporized from the dieltrin-water surface in the saturation chamber at the rate of approximately 0.35 ng. per sq. cm. per minute, or approximately 0.05 pound per acre per day. At this flow rate the air flow across the water surface in the relatively large saturation chamber was only 15 cm. per minute, or less than 0.006 m.p.h. At air-flow rates encountered under field conditions, the potential rate of volatilization would be considerably higher.

The fact that water covering the HEOD in the saturation chamber did not affect the vapor density and that relatively low concentrations in soil resulted in the same vapor density as the pure material while not losing moisture, would indicate that the evaporation of water does not contribute to increased vapor density, or "potential volatility." The reported discrepancies between volatilization rates from water surfaces and those predicted from vapor pressure measurements may be partly due to the presence of much higher vapor densities than predicted from vapor pressure measurements based on effusion or other techniques not involving direct measurements of concentration of the material in the vapor phase.

Studies continue on the concentration in soil at which vapor density falls below the saturation value, and on factors affecting actual volatilization rates, such as soil-water content, temperature, and soil characteristics.

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